

METHOD AND APPARATUS FOR TREATING  
A FLUOROCOMPOUND-CONTAINING GAS STREAM

The present invention relates to gas abatement. The invention finds particular use in the abatement of gases exhaust from a process tool used in the semiconductor manufacturing industry.

CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, NF<sub>3</sub> and SF<sub>6</sub> are commonly used in the semiconductor manufacturing industry, for example, in dielectric film etching. Following the manufacturing process there is typically a residual perfluorocompound (PFC) content in the effluent gas pumped from the process tool. PFCs are difficult to remove from the effluent gas, and their release into the environment is undesirable because they are known to have relatively high greenhouse activity.

The object of abatement is to convert the PFCs into one or more compounds that can be more conveniently disposed of, for example, by conventional scrubbing.

Plasma abatement has proved to be an effective method for degradation of PFCs to less damaging species. In the plasma abatement process, an effluent gas containing the PFCs to be destroyed is caused to flow into a high density plasma. Under the intensive conditions within the plasma, the PFCs are subjected to impact with energetic electrons causing dissociation into reactive species. These species can combine with oxygen or hydrogen added to the effluent gas to produce relatively stable, low molecular weight by-products, for example, CO, CO<sub>2</sub> and HF, which can then be removed in a further treatment step utilising, for example, a wet scrubber to take the HF into aqueous solution.

However, known plasma abatement techniques tend to be relatively complex and have relatively high energy requirements. For example, in one known plasma abatement technique, the effluent gas stream is conveyed into a

resonant cavity using microwave radiation to generate, from the PFCs, a microwave plasma. Another known technique is to convey the effluent stream into a dielectric tube, a high frequency surface-wave exciter being used to produce surface waves which generate a plasma within the tube to  
5 dissociate the PFCs.

In another PFC abatement technique, the effluent waste stream is brought into contact with a superheated stream of water vapour for reacting with the PFCs within the waste stream. However, such a technique not only requires  
10 heating of the water vapour to a temperature of at least 150°C, but also requires the effluent stream to be subsequently conveyed through a heat exchange mechanism to cool the stream before it is conveyed to a wet scrubber, the efficiency of the scrubber decreasing as a function of increasing temperature.

15 It is an aim of at least the preferred embodiment of the present invention to provide a relatively simple and efficient technique for treating a fluorocompound-containing stream.

20 In a first aspect, the present invention provides a method of treating a fluorocompound-containing gas stream, the method comprising generating a plasma stream from a plasma source gas, injecting the generated plasma stream through an aperture into a chamber, conveying to the plasma stream a source of  $\text{OH}^-$  and/or  $\text{H}^+$  ions for impinging upon the plasma stream to form  
25 heated ions, and conveying the gas stream to the heated ions.

As used herein, the term "fluorocompound" means any species comprising fluorine, and includes fluorocarbons, perfluorocompounds and hydrofluorocompounds, such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ , and  $\text{C}_4\text{F}_8$ , that can be  
30 converted into  $\text{CO}_2$  and  $\text{HF}$ , which can be taken into solution in a wet scrubber. Other examples are  $\text{NF}_3$ , which can be converted into  $\text{N}_2$  and  $\text{HF}$ , and  $\text{SF}_6$ , which can be converted into  $\text{SO}_2$  and  $\text{HF}$ .

By providing a method in which heated  $\text{OH}^-$  and/or  $\text{H}^+$  ions are formed from a suitable source thereof, such as water or an alcohol, for subsequent reaction with a PFC component in an effluent gas stream, it has been found that the energy required to cause the destruction of the PFC component of the gas stream can be reduced, and the efficiency of that destruction can be radically improved. For example,  $\text{H}^+$  and  $\text{OH}^-$  ions formed from the dissociation of water are capable of reacting with a PFC contained in the gas stream within a reaction chamber at ambient temperature, and thus at a much lower temperature than would be required if the water had not been pre-ionised before being introduced into the waste stream.

By injecting the plasma stream into the chamber through an aperture, another advantage is provided by not bringing the equipment used to generate the plasma stream into contact with either the effluent gas stream or any by-products from the reaction of the PFC with the  $\text{OH}^-$  and/or  $\text{H}^+$  ions. As a result, any one of a range of equipment may be used to generate the plasma stream. In the preferred embodiment, a plasma is generated to decompose a plasma source gas to produce the plasma stream. For example, the plasma may be generated using a D.C source or radiation at a frequency of around 580 kHz, 13.56 MHz, 27 MHz, 915 MHz or 2.45 GHz to generate a plasma stream from the plasma source gas. Alternatively, a glow discharge may be generated to decompose the source gas. As is well known, a glow discharge is a luminous, thermal plasma formed by applying to a gas a voltage that is greater than the breakdown voltage of that gas. The plasma stream may also be generated by a discharge other than a glow discharge, for example by a corona discharge or an arc discharge. Such a discharge may be generated using a plasma gun, in which an electric arc is created between a water-cooled nozzle (anode) and a centrally located cathode. A stream of source gas, for example, an inert, ionisable gas such as nitrogen or argon, passes through the electric arc and is dissociated thereby. The plasma stream issuing from the nozzle resembles an open oxy-acetylene flame.

The plasma stream thus provides a dual role of (a) generating adequate species in the form of  $H^+$  and/or  $OH^-$  ions that would then react with the PFC component of the gas stream, and (b) imparting heat as the initiation energy that enables the reaction between the ions and the PFC.

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Further advantages are that a relatively cheap and readily available fluid, such as water vapour or a fuel, for example hydrogen, hydrocarbon or an alcohol, can be used to generate  $H^+$  and/or  $OH^-$  ions, and that the reaction can take place at any convenient pressure, for example, around or below atmospheric pressure. Examples of a suitable alcohol include methanol, ethanol, 10 propanol, propan-2-ol and butanol. Other examples of a source of  $H^+$  ions include hydrogen, a hydrocarbon, ammonia and a paraffin.

Various techniques may be used to form the ions using a plasma gun. In a 15 first technique, a plasma stream is formed and, prior to the injection of the plasma stream into the chamber, water (as an example of a suitable source of these ions) is conveyed to the stream so that a flame containing these ions is injected into the chamber to abate the effluent gas stream within. The water may be conveyed to the plasma stream separately from the source gas, or 20 within a fluid mixture comprising both water vapour and the source gas. In a second technique, both water and the effluent gas stream are separately conveyed into the chamber. The water is dissociated by the flame to form heated ions within the chamber, which ions subsequently react with the PFC component of the waste stream. In a third technique, the effluent gas stream 25 is conveyed to the plasma stream prior to its injection into the reaction chamber, so that both the plasma stream and the gas stream, which may comprise the PFC and/or radicals generated from the PFC, are injected into the reaction chamber. Water may be conveyed to the plasma stream upstream from the aperture, that is, with one of the source gas or the effluent 30 gas stream, or separately therefrom, or may be conveyed to the plasma stream downstream from the nozzle, for example, directly to the reaction chamber. In this case, the water may impinge upon the plasma stream to

form heated ions within the chamber for reacting with the PFC and/or the PFC radicals, and/or may react directly with the PFC radicals within the chamber for abatement thereof. Thus, in a second aspect the present invention provides a method of treating a fluorocompound-containing gas stream, the method comprising generating a plasma stream from a plasma source gas, adding the gas stream to the plasma stream, injecting the plasma stream and gas stream through an aperture into a reaction chamber, and conveying to the plasma stream a source of  $\text{OH}^-$  and/or  $\text{H}^+$  ions.

In the preferred embodiment, a single plasma gun is used to inject the plasma stream into the reaction chamber. However, a plurality of such guns may be provided to inject a plurality of plasma streams into the same chamber, each for abating a common or respective gas stream. Alternatively, a plurality of gas streams may be conveyed to a single chamber, into which a single plasma stream is injected. This can increase further the efficiency of the treatment of the waste stream. These guns may be connected to a common power source or to respective sources.

Depending on whether the chamber is connected to the inlet or the outlet of a pump for pumping the gas stream from, for example, a process tool, and the flow rate of the gas stream, the chamber may be at any pressure in the range from  $10^{-3}$  mbar to 2000 mbar.

Depending on the nature of the reaction occurring within the chamber, the abatement of the fluorocompound within the gas stream may be promoted by heating the chamber, for example, to a temperature in the range from ambient to  $1500^\circ\text{C}$ . For example, the chamber may be heated to a temperature in the range from  $400^\circ\text{C}$  to  $1500^\circ\text{C}$ , more preferably in the range from  $500^\circ\text{C}$  to  $1000^\circ\text{C}$ .

The ion source may be injected into the chamber over a catalyst, for example, one of tungsten, silicon and iron.

The gas stream is preferably subsequently conveyed to a wet scrubber or a reactive solid media downstream from the chamber to remove one or more by-products from the reaction from the gas stream. The scrubber may be coupled close to the reaction chamber, or may be more remote from the  
5 reaction chamber.

As previously mentioned, the PFC may comprise a perfluorinated, or a hydrofluorocarbon, compound, for example, one of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$ ,  $\text{NF}_3$  and  $\text{SF}_6$ .  
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In a third aspect, the present invention provides apparatus for treating a fluorocompound-containing gas stream, the apparatus comprising a reaction chamber, means for generating a plasma stream from a plasma source gas and injecting the generated plasma stream through an aperture into the  
15 chamber, means for conveying to the plasma stream a source of  $\text{OH}^-$  and/or  $\text{H}^+$  ions for impinging upon the plasma stream to form heated  $\text{OH}^-$  and/or  $\text{H}^+$  ions, and means for conveying the gas stream to the heated ions.

In a fourth aspect, the present invention provides apparatus for treating a  
20 fluorocompound-containing gas stream, the apparatus comprising a reaction chamber, means for generating a plasma stream from a plasma source gas, means for conveying the gas stream to the plasma stream, means for injecting the plasma stream and gas stream through an aperture into the reaction chamber, and means for conveying to the plasma stream a source of  
25  $\text{OH}^-$  and/or  $\text{H}^+$  ions.

The invention also provides a method of treating an effluent fluid stream from a semiconductor manufacturing process tool, the method comprising injecting an ionised fluid stream into a reaction chamber, and conveying the effluent  
30 fluid stream to the chamber, wherein the ionised fluid stream either contains reactive species for reacting with a component of the effluent fluid stream, or

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impinges upon a reactive fluid conveyed to the chamber to form the reactive species.

Features described above in relation to method aspects of the invention are  
5 equally applicable to apparatus aspects, and vice versa.

Preferred features of the present invention will now be described with reference to the accompanying drawings, in which:

10 Figure 1 illustrates schematically one example of a processing system;

Figure 2 illustrates schematically another example of a processing system;

Figure 3 illustrates the fluid supply to the plasma abatement device of the  
15 processing systems of Figure 1 or Figure 2;

Figure 4 illustrates in more detail the plasma abatement device of Figure 3;

Figure 5 is an illustration of one embodiment of a plasma torch suitable for  
20 use in the device of Figure 4;

Figure 6 illustrates the use of the torch of Figure 5 with a plurality of gas streams entering the abatement device;

25 Figure 7 is an illustration of a second embodiment of a plasma torch suitable for use in the device of Figure 4;

Figure 8 illustrates a third embodiment of a plasma torch suitable for use in the device of Figure 4; and

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Figure 9 illustrates a fourth embodiment of a plasma torch suitable for use in the device of Figure 4.

With reference first to Figure 1, a processing system for processing, for example, semiconductor or flat panel display devices, comprises a processing chamber 10 of a processing tool that receives various gases (not shown) for use in performing the processing within the chamber. One example of a  
5 processing tool is a plasma etch reactor, which receives an etchant gas for performing plasma etching of semiconductor wafers located within the processing chamber 10. Examples of suitable etchant include the perfluorocompounds (PFCs) having the general formula  $C_xF_y$  where  $x \geq 1$  and  $y \geq 1$ , such as  $CF_4$ ,  $C_2F_6$ ,  $C_3F_8$ , and  $C_4F_8$ , although other etchants including  
10 hydrofluorocarbon gases, such as  $CHF_3$ ,  $C_2HF_5$  and  $CH_2F_2$ ,  $NF_3$ , and  $SF_6$  may be used. Other gases supplied to the processing chamber 10 may include oxygen as a reactant for reacting with the etchant, and unreactive noble gases, such as argon and helium.

15 An effluent gas stream is drawn from the outlet of the process chamber 10 by a pumping system. During the etching process, only a portion of the reactants will be consumed, and so the effluent gas stream exhaust from the outlet of the process chamber 10 will contain a mixture of the reactants, the unreactive noble gases supplied to the chamber, and by-products from the etch process.

20 The pumping system comprises a secondary pump 12, typically in the form of a turbomolecular pump, for drawing the effluent stream from the process chamber 10. The turbomolecular pump 12 can generate a vacuum of at least  $10^{-3}$  mbar in the process chamber 10. The effluent stream is typically  
25 exhausted from the turbomolecular pump 12 at a pressure of around 1 mbar. In view of this, the pumping system also comprises a primary, or backing pump 14 for receiving the effluent stream exhaust from the turbomolecular pump 12 and raising the pressure of the effluent stream to a pressure around atmospheric pressure.



In order to remove the harmful PFC components from the effluent stream, the effluent stream is conveyed through a plasma abatement device 16. As illustrated in Figure 1, the abatement device 16 may be located between the turbomolecular pump 12 and the backing pump 14, with the abatement thus being performed at a sub-atmospheric pressure, or, as illustrated in Figure 2, the abatement device 16 may be connected to the exhaust from the backing pump, with the abatement thus being performed at or around atmospheric pressure.

Figure 3 illustrates the gas supplies to the abatement device 16. The effluent stream is conveyed to a first inlet 18 of the abatement device 16 by conduit 20, and is conveyed from the outlet 22 of the abatement device 16 by conduit 24. A source of  $\text{OH}^-$  and/or  $\text{H}^+$  ions, in this example water, is supplied from a source 26 thereof to a second inlet 28 of the abatement device 16 by conduit 30, and an ionisable, plasma source gas, in this example nitrogen, is supplied from a source 32 thereof to a third inlet 34 of the abatement device by conduit 36.

With reference to Figure 4 the abatement device 16 comprises a reaction chamber 40 in which are formed the first inlet 18 for receiving the effluent stream, the second inlet 28 for receiving the ion source, and the outlet 22 for exhausting from the chamber 40 a fluid stream containing by-products from the abatement process and other, unabated gases contained within the effluent stream entering the abatement device 16. The abatement device 16 further comprises a dc plasma torch 42 for receiving the nitrogen stream from the conduit 36 and generating a plasma stream that is injected into the chamber 40 in the form of a flame emitted from an aperture or nozzle 44 of the plasma torch 42. As shown in Figure 4, the plasma torch 42 also receives a flow of water coolant that enters and leaves the torch via a conduit system indicated generally at 46 in Figure 4.

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Figure 5 shows in more detail the configuration of one embodiment of the plasma torch 42. The plasma torch 42 comprises an elongate tubular cathode, or electron emitter, 48 having an end wall 50. Water coolant is conveyed through the bore 52 of the electron emitter 48 during use of the plasma torch 42. The bore 52 of the electron emitter 48 is aligned with the nozzle 44 formed in a start anode, or electrode 54 surrounding the end wall 50 of the electron emitter 48. The start electrode 54 is mounted in an insulating block 56 surrounding the electron emitter 48. A bore formed in the insulating block 56 provides the third inlet 34 of the abatement device, and conveys a stream of plasma source gas into a cavity 58 located between the end wall 50 of the electron emitter 48 and the start electrode 54.

In operation of the plasma torch 42, a pilot arc is first generated between the electron emitter 48 and the start electrode 54. The arc is generated by a high frequency, high voltage signal typically provided by a generator associated with the power supply for the torch. This signal induces a spark discharge in the plasma source gas flowing in the cavity 58, and this discharge provides a current path. The pilot arc thus formed between the electrode emitter 48 and the start electrode 54 ionises the plasma source gas passing through the nozzle 44 to produce a high momentum plasma flame of ionised source gas from the tip of the nozzle 44. The flame passes from the nozzle towards a secondary anode 60 surrounding the nozzle 44 to define a plasma region 62. The secondary anode 60 may be provided by part of the wall of the chamber 40, or may be a separate member inserted into the chamber 40, in which case the secondary anode 60 may be provided with apertures 64, 66 which align with the inlets 18, 28 of the chamber 40 to enable the ion source and the effluent stream to be conveyed to the plasma region 62. The lower (as illustrated) portion of the secondary anode 60 may be profiled as shown in Figure 5 to enable the secondary anode to be used instead of the start electrode 54 to generate the plasma stream from the plasma source gas.

In use, the ion source, in this example water, is dissociated by the plasma flame emitted from the nozzle 44 of the torch plasma 42 to form  $H^+$  and  $OH^-$  ions within the plasma region 62. These ions subsequently react within the chamber 40 with the PFC component(s) of the effluent stream entering the chamber 40. The by-products from the reaction, and any unabated noble gases contained within the effluent stream entering the chamber 40, are exhaust from the chamber 40 through outlet 22, and subsequently conveyed to a wet scrubber, solid reaction media, or other secondary abatement device 70, as illustrated in Figures 1 and 2. After passing through the abatement device 70, the effluent stream may be exhaust to the atmosphere.

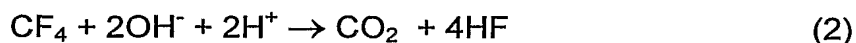
Some examples of reactions occurring within the chamber 40 will now be described.

#### Example 1

The reactive fluid is a source of  $H^+$  and  $OH^-$  ions, for example, water vapour, and the effluent stream contains a perfluorocompound, for example,  $CF_4$ . The plasma flame dissociates the water vapour into  $H^+$  and  $OH^-$  ions:



which react with  $CF_4$  to form carbon dioxide and HF as by-products:



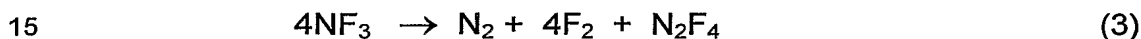
The HF contained within the stream exhaust from the abatement device can be taken into aqueous solution within the wet scrubber, or reacted with a solid reaction media to form a solid by-product which can be readily disposed of.

A typical gas mixture for performing a dielectric etch in a process tool may contain differing proportions of the gases  $CHF_3$ ,  $C_3F_8$ ,  $C_4F_8$  or other

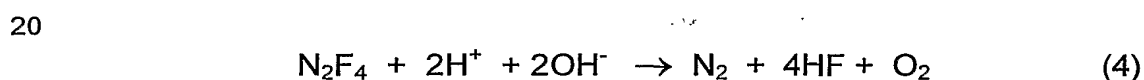
perfluronated or hydrofluorocarbon gas, but the chemical reactions of the  $H^+$  and  $OH^-$  ions with these components of the waste gas stream will differ in detail but the general form will be as the scheme above.

5     Example 2

The reactive fluid is again a source of  $H^+$  and  $OH^-$  ions, for example, water vapour, and the waste stream contains  $NF_3$ . Process tool manufacturers are increasingly adopting  $NF_3$  as the chamber cleaning gas of choice for PECVD  
10    reactors. Whereas the utilisation of  $NF_3$  by the cleaning process is much higher than that of either  $CF_4$  or  $C_2F_6$ , the by-products produced are considerably more reactive and their uncontrolled release is potentially very dangerous. Within the plasma,  $NF_3$  dissociates to form  $N_2$ ,  $F_2$  and  $N_2F_4$ :



with the  $N_2F_4$  component of the effluent stream subsequently reacting with the  $H^+$  and  $OH^-$  ions generated from the impingement of the water vapour on the plasma flare:



to form by-products that can be readily disposed of.

25     Example 3

It is normal practice to introduce materials such as silicon, phosphorus, arsenic into a process tool as both inorganic hydrides or organometallic compounds. Other materials such as silicon, tantalum, aluminium, copper are  
30    introduced into the process chamber as organometallic compounds. In other process steps by-products of reaction are known to make powders that are very reactive and present a substantial danger if they collect in quantity, as

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they have been known to spontaneously react causing equipment damage. The introduction of reactive ions directly into the waste gas has been shown to substantially reduce the reactivity of such compounds, rendering them safe for subsequent handling.

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The reactions are further enhanced by maintaining the reaction chamber at an elevated temperature in the range of 400°C to 1500°C, but preferably in a temperature range 500°C to 1000°C.

10 As illustrated by the above examples, the same ions may be used to remove various different components from a gas stream. Consequently, the abatement device is suitable to receive a plurality of gas streams, either from similar or different process tools, and convert similar or different components of those gas streams into species that can be treated by the secondary  
15 abatement device 70. For example, as illustrated in Figure 6, the abatement device may be provided with an additional inlet for receiving an additional gas stream via conduit 20a, with an additional aperture 64a being provided in the secondary anode 60 to enable the additional gas stream to be conveyed to the plasma region 62.

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In Example 1 above, the ions react with the CF<sub>4</sub> component of the effluent stream entering the chamber 40, and so it is not essential for the effluent stream to pass through the plasma flare to decompose the CF<sub>4</sub> prior to reaction with the ions. In contrast, in Example 2 above, it is desirable to  
25 convey the effluent stream through the plasma stream in order to dissociate the NF<sub>3</sub> into species that are more reactive with the ions generated by the ion source. In the examples illustrated in Figures 4 to 6, the effluent stream may be conveyed into the chamber 40 proximate the plasma region 62 so that the PFC passes through the plasma region. Figure 7 illustrates an example of a  
30 plasma torch 80 in which the contact of the effluent stream with the plasma flare is maximised. In this example, the effluent stream is conveyed directly to

the plasma torch 80, rather than into the reaction chamber 40. As shown in Figure 7, the effluent stream is conveyed from the first inlet 18 of the abatement device into the bore 52 of the electron emitter 48. The effluent stream passes from the open end 82 of the electron emitter 48 into the cavity 58 between the electron emitter 48 and the start electrode 54 of the plasma torch 80. The cavity 58 also receives a stream of plasma source gas entering the abatement device through the third inlet 34 formed in the electrically insulating block 56 surrounding both the electron emitter 48 and the start electrode 54.

In use, similar to the example illustrated in Figure 5, a pilot arc is first generated between the electron emitter 48 and the start electrode 54 by supplying a high frequency, high voltage signal to a hafnium insert 84. The pilot arc thus formed between the electrode emitter 48 and the start electrode 54 ionises the plasma source gas entering the cavity 58 from the third inlet 34 to produce a high momentum plasma flame of ionised source gas from the tip of the nozzle 44. As the effluent stream enters the cavity 58 from the open end 82 of the electron emitter 48, it mixes with the plasma source gas within the cavity 58 and is emitted from the nozzle 44 with the plasma stream into the plasma region 62. Water is supplied to the plasma region 62 from the second inlet 28, which in this example is also formed in the insulating block 56 of the torch 42. The water is decomposed by the plasma stream to form  $H^+$  and  $OH^-$  ions, which react with the PFC, and/or with species formed from the dissociation of the PFC by the plasma stream, within the reaction chamber.

It is to be understood that the foregoing represents various examples of the invention, others of which will no doubt occur to the skilled addressee without departing from the true scope of the invention as defined by the claims appended hereto.

For example, whilst in the illustrated examples the plasma abatement device 16 has three separate inlets each for receiving a respective one of the effluent

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stream, ion source and plasma source gas, the number of inlets may be reduced by conveying, for example, the plasma source gas to the plasma torch in a stream also containing the ion source. Figure 8 illustrates a modification of the plasma torch shown in Figure 5 where the plasma source gas and the ion source are both conveyed to the plasma torch 42 through the inlet 34. Alternatively, as illustrated in Figure 9, the second inlet 28 may be configured to supply the ion source directly to the cavity 58 located between the electrodes 48, 54 of the plasma torch. In both of these modifications, the ion source enters the reaction chamber 40 through the nozzle in a dissociated state, that is, with the plasma stream injected into the reaction chamber containing the ions for reacting with the fluorocarbon component of the gas stream. Similarly, in the embodiment shown in Figure 7, the ion source may be conveyed to the plasma torch 80 with the plasma source gas, or it may be conveyed to the cavity 58 separately from the plasma source gas. As another alternative, the ion source may be conveyed to the plasma torch 80 mixed with the effluent stream, as under normal conditions the ion source is not reactive with the PFC component of the effluent stream.